

or intramolecular addition⁸ to double bonds could be detected. The ratios of the dimers to the hydrogenated products formed in the reaction of phenylethylenes **1a-c**, **2**, and **7a** were 10, 4, and 3, respectively. In the reaction of alkylethylenes, the corresponding ratios were lower: between 1.4 and 0.8 for **7b-d** and 0.3 for **7e**. Methylene derivatives **1a-c** reacted faster than all other olefins: after 30 min reaction at -78 °C, the former were converted almost completely to products, while the latter only in 40-50%.

The pattern of these reactions and the ratios of the products are consistent with the formation of radicals which undergo dimerization and disproportionation, as well as addition of H atoms.⁹ We have shown that the latter two processes take place by reacting cyclohexene with D atoms and isolating cyclohexane-*d*₂ (40%) and -*d*₁ (60%), the former being mainly the product of D-addition to the cyclohexyl radical and the latter of its disproportionation.

When the reactions of H with olefins were performed in toluene, combination products of olefins and toluene were also formed. Thus, **1b** in toluene (5%) gave, after 1 h at -78 °C, 20% yield of three compounds **10a**, **11a**, and **12a**¹⁰ in 2:1:1 ratio. They were separated after treatment with 2-phenyltriazoline-1,3-dione, resulting in adducts from which **11a** and **12a** were regenerated with KOH. Dehydrogenation of **11a** with dichlorodicyanobenzoquinone (DDQ) led to the metasubstituted toluene **13a**.¹¹

Analogous three methylcyclohexadiene derivatives **10b**, **11b**, and **12b**¹² were formed (in 8:1:1 ratio) in the reaction of **7b** in toluene with H atoms. The major product **10b** was dehydrogenated with DDQ to the meta-substituted toluene derivative **13b**.¹³ The formation of small amounts of dimers derived from self-condensation of hydrogenated toluene was indicated by the isolation of biphenyl derivative **13c** after dehydrogenation of the total reaction mixture.

Neat toluene also reacted with H atoms, resulting, after 30 min of reaction (ca. 1% conversion), in a mixture of dimeric products whose main constituent was a bicyclohexyl derivative **10d**.¹⁴ It is apparent that **10-12** are thus all derived from methylcyclohexadienyl radical formed by the addition of H atom to the ortho position of toluene.

Theoretical calculation by Radom et al.¹⁵ has shown that the latter radical is the thermodynamically most stable of the four isomeric methylcyclohexadienyl radicals. Since it was previously established that H atoms add to ortho, meta, and para positions of toluene,¹⁶ the exclusive addition to the ortho position observed

by us implies equilibration between the isomeric radicals, which occurs by elimination of H atoms, followed by their addition. Such equilibria seem reasonable in view of the reported data on the reactions of toluene and substituted toluenes with D atoms in solution² and on the thermal dissociation of cyclohexadienyl radical to benzene and H atoms in the gas phase.¹⁷

Evidence for equilibration of methylcyclohexadienyl radicals was obtained from the reaction of toluene with deuterium atoms, which results in ca. 10% of toluene-*d*₁ and ca. 1% of the mixture of dimeric products. We are presently investigating the scope and the synthetic application of these meta substitutions in benzene derivatives.

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Control of Stereochemistry in Five-Coordinate d⁶ Complexes by Ligand Substitution

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There is overwhelming evidence from both theoretical studies² and solid-state structural analyses³ that five-coordinate d⁶ complexes prefer the square-pyramidal geometry over the isomeric trigonal-bipyramidal form. Thus complexes of Ru(II),⁴ Os(II),⁴ Rh(III),⁵ and Ir(III),⁶ when five-coordinate, are generally assumed to be square pyramidal in spite of the fact that solution studies rarely^{7,8} provide unequivocal support for this assumption. In this paper, we detail a five-coordinate d⁶ system for which both isomeric forms are observed as a function of the ligand substitution; moreover, we present a compelling diagnostic method that distinguishes between the two possible isomeric forms *in solution*.

A previous report from our laboratory outlined the preparation of the dark-green methyl halide complexes Ir(CH₃)X[N-(SiMe₂CH₂PPh₂)₂] (X = I, **1a**; X = Br, **1b**). These five-coordinate complexes are square pyramidal¹⁰ both in the solid state, based on the X-ray structure of an analogue (i.e., Ir(CH₃)I[N-(SiMe₂CH₂P(i-Pr)₂)₂]), and in solution, based on variable-temperature ¹H NMR studies, ligand addition reactions, and NOE-DIFF¹¹ experiments. In particular, the observation of a positive

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(10) **10a**: MS, *m/e* (relative intensity) 91 (100%), 51 (21), 77 (78), 93 (88), 105 (82), 119 (50), 120 (62); ¹H NMR (270 MHz, CDCl₃) δ 7.1-7.3 (m), 5.75 (d, *J* = 10.7 Hz, 1 H), 5.45 (m, 1 H), 5.22 (m, 1 H), 3.02 (br, 1 H), 2.47 (br s, 2 H), 1.65 (s, 3 H), 1.25 (d, *J* = 4 Hz, 6 H). **11a**: MS, *m/e* (relative intensity) 93 (100%), 51 (18), 77 (60), 91 (99), 105 (83), 119 (58), 120 (68); ¹H NMR (270 MHz, CDCl₃) δ 7.02-7.35 (m, 5 H), 5.83 (ddd, *J* = 9.8, 5.2, 2.6 Hz, 1 H), 5.42 (dd, *J* = 13, 3.3 Hz, 1 H), 5.55 (br, 1 H), 2.7 (br, 1 H), 1.91 (m, 2 H), 1.69 (s, 3 H), 1.27 (d, *J* = 5 Hz, 6 H). **12a**: ¹H NMR (270 MHz, CDCl₃) δ 7.1-7.4 (m), 5.55-5.82 (m, 4 H), 2.55 (dt, *J* = 17.5, 5 Hz, 1 H), 1.73 (dd, *J* = 5.2, 5 Hz, 1 H), 0.92 (s, 3 H), 1.36 (d, 6 H).

(11) **13a**: MS, *m/e* (relative intensity) 195 (100%), 77 (39), 89 (40), 91 (42), 103 (51), 165 (18), 210 (M⁺, 27); ¹H NMR (90 MHz, CD₂Cl₂, 5.31 ppm) δ 7.22 (m, 3 H), 7.02 (m, 2 H), 2.3 (s, 3 H), 1.67 (s, 6 H).

(12) **10b**: product of reaction with deuterium atoms; ¹H NMR (270 MHz, CDCl₃) 5.75 (d, *J* = 10.7 Hz, 1 H), 5.62 (d, *J* = 10.7 Hz, 1 H), 5.33 (d, 1 H), 2.62 (br, 1 H), 2.50 (br, 2 H), 1.68 (s, 3 H), 1.14 (br, 10 H); MS, *m/e* 54 (100), 56 (11), 78 (17), 92 (49), 93 (42), 178 (M⁺, 7). **11b** and **12b** identified as a mixture of endo and exo adducts with 2-phenyltriazoline-1,3-dione. **11b**: adduct a; ¹H NMR (270 MHz, CDCl₃) 7.45 (m, 5 H), 6.49 (m, 1H), 6.28 (br s, 1H), 4.98 (br s, 1H) 1.92 (s, 3H), 0.85-2 (m, 5H); adduct b; ¹H NMR (270 MHz, CDCl₃) δ 7.5 (m, 5 H), 6.34 (m, 2 H), 5.02 (br s, 1 H), 1.92 (s, 3 H), 0.9-2.25 (m, 14 H).

(13) **13b**: ¹H NMR (80 MHz, CDCl₃) 7.53-7.02 (m, 4 H), 2.3 (s, 3 H), 1.81-0.88 (m, 11 H).

(14) **10d**: meso and *dl*; MS, *m/e* (relative intensity) 93 (100%), 91 (60), 79 (47), 77 (63), 65 (20); MS-Cl (relative intensity) 187 (M⁺, 100%), 151 (25), 137 (27), 119 (10), 115 (31); ¹H NMR (270 MHz, CDCl₃) δ 5.76 (br, 1 H), 5.31 (br, 1 H), 2.85 (br, 1 H), 2.55 (br s, 2 H), 1.69 (s, 6 H).

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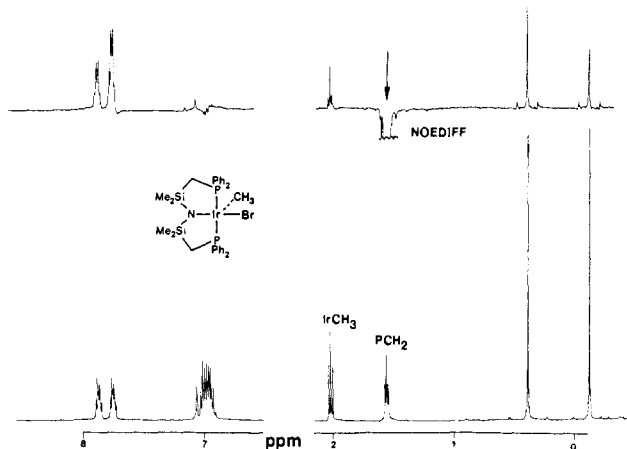


Figure 1. ¹H NMR spectrum (bottom), 400 MHz, and NOEDIFF spectrum (top) for the methyl bromide complex **1b**; irradiation of the methylene protons of the ligand backbone results in a positive NOE for the iridium methyl protons.

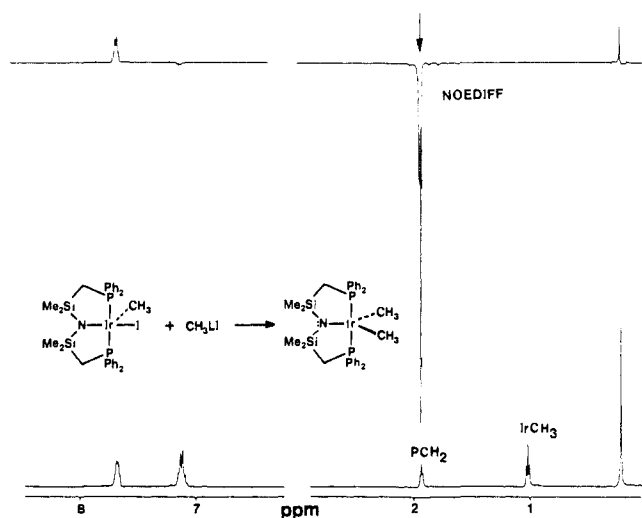


Figure 2. ¹H NMR spectrum (bottom), 400 MHz, and NOEDIFF spectrum (top) for the dimethyl complex **2**; irradiation of the methylene protons of the ligand backbone results in no detectable NOE for the iridium methyl protons.

nuclear Overhauser effect¹² (NOE), as shown in Figure 1, for the iridium methyl proton resonance upon irradiation of the methylene protons of the ligand backbone requires that the methyl ligand be apical and cis disposed to the amide nitrogen donor; as will be discussed below, this result is important in light of the contrasting NOEDIFF results obtained for the dialkyl derivatives.

The deep red or purple methyl alkyl complexes Ir(CH₃)R[N(SiMe₂CH₂PPh₂)₂] (R = CH₃, **2**; CH₂CMe₃, **3**; CH₂SiMe₃, **4**; CH₂Ph, **5**) are prepared from the methyl iodide complex **1** as previously described.¹³ The ¹H NMR spectrum of the dimethyl derivative **2** (Figure 2) shows only one resonance for both of the iridium methyl groups (Ir(CH₃)₂) as well as one singlet for the silylmethyl protons and a virtual triplet for the methylene hydrogens (PCH₂Si) even down to -100 °C; upon irradiation of the methylene resonance, no NOE is detected for the iridium methyl

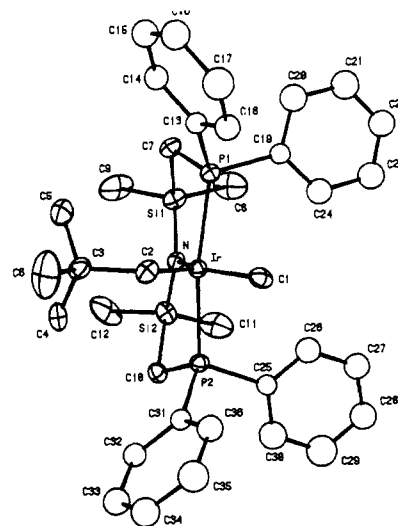


Figure 3. Perspective view of one molecule with numbering scheme. Geometry (Å and deg); Ir-P1 2.308 (2), Ir-P2 2.303 (2), Ir-N 2.109 (7), Ir-Cl 2.131 (9), Ir-C2 2.089 (9); N-Ir-Cl 152.5 (3), N-Ir-C2 131.5 (3), Cl-Ir-C2 76.0 (4), P1-Ir-P2 168.45 (9), N-Ir-P1 88.2 (2).

protons. Given the results¹⁴ found for the methyl halide complexes **1**, the failure to observe a significant NOE (positive or negative) implies that a different stereochemistry than square pyramidal exists for the dimethyl complex **2**; a trigonal-bipyramidal structure is therefore invoked. This rationale is based on the accepted origin¹² of the NOE as a through-space transfer of magnetization that varies as 1/*r*⁶; thus in the square-pyramidal geometry, the apical methyl group is *closer* to the methylene protons of the ligand backbone than in a trigonal-bipyramidal form where the methyl group is in the equatorial plane. That the tridentate ligand itself is not the source of the difference in the two isomers is evident from the similar NOE's observed for the ortho protons of the phenyl substituents on the phosphorus donors (i.e., enhancements at 7.9 and 7.8 ppm in Figure 1, and at 7.7 ppm in Figure 2).

Additional persuasive evidence that these two five-coordinate systems have different ground-state geometries is the X-ray crystal structure¹⁵ of the methyl neopentyl derivative **3** shown in Figure 3. Although distorted, the geometry is best described as a trigonal bipyramid; to our knowledge, this is the first five-coordinate Ir(III) complex structurally characterized as trigonal bipyramidal. The ¹H NMR spectrum of **3** follows exactly the pattern of the dimethyl complex **2** especially in the lack of an observable NOE in the protons of both the methyl (IrCH₃) or the neopentyl methylene (IrCH₂CMe₃) ligands when the ligand methylene protons are irradiated. These NOE results are similarly observed for the other methyl alkyl derivatives **4** and **5**, as well as the related dibenzyl complex Ir(CH₂Ph)₂[N(SiMe₂CH₂PPh₂)₂]¹⁶ and the diphenyl derivative Ir(Ph)₂[N(SiMe₂CH₂PPh₂)₂].¹⁶

As already mentioned, the observation of a trigonal-bipyramidal geometry for these Ir(III) systems both in the solid state and in solution would appear to contradict the current theoretical dogma.² In fact, there is an obscure but excellent paper¹⁷ by Thorn and

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(14) Similar NOE's are observed for the corresponding benzyl halide derivatives Ir(CH₂Ph)X[N(SiMe₂CH₂PPh₂)₂] (X = Cl and Br) and phenyl halide complexes Ir(Ph)X[N(SiMe₂CH₂PPh₂)₂] (X = Cl, Br, and I), all of which are square pyramidal.¹⁶

(15) X-ray data of the methyl neopentyl complex **3**. The molecule crystallizes in space group *P*¹ with *a* = 15.809 (3) Å, *b* = 16.849 (5) Å, *c* = 15.736 (7) Å; α = 96.39 (3)°, β = 95.57 (3)°, γ = 66.62 (2)°; *V* = 3817 Å³, and *Z* = 4 (two independent). Data collected at 23 °C on a CAD4F diffractometer. Structure solved by using Patterson techniques on an SDP structure solution system. Final *R* factors, by full-matrix least-squares refinement on *F*, of 0.049 and 0.060 for 6974 reflections with *I* > 3σ(*I*). All non-H atoms, other than the C atoms of the phenyl rings, refined with anisotropic thermal parameters for a total of 517 parameters. Tables of atomic positional and thermal parameters and bond distances and angles are available as supplementary material. Complete crystallographic details of this and other related structures will be published at a later date.

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Hoffmann that predicts all of the results described above, even though their analysis was directed toward d^6 metallocycles and related systems. Two relevant conclusions from their theoretical calculations are (i) a trigonal-bipyramidal structure should be preferred if a single-faced π -donor (i.e. amide, NR_2^-) is present and (ii) strong σ -donors (i.e., alkyl ligands) will prefer the equatorial sites with a decrease in the angle between these donors (from 120° to 90°). This latter point is clearly apparent in the structure shown in Figure 3 wherein the C1-Ir-C2 angle is $76.0(4)^\circ$. Thus, the replacement of a halide moiety, a good double-faced π -donor, with a strong σ -donor such as an alkyl ligand causes a sufficient perturbation to interchange the relative stabilities of the ground-state geometries for these five-coordinate d^6 complexes.

Equipped with the knowledge of the solution stereochemistry of these dialkyl derivatives, we are now in a position to address the mechanism of the photoinduced α -elimination process previously reported for these compounds.^{13,18}

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Supplementary Material Available: Experimental details, ^1H NMR data, and analytical data for all new compounds, tables of bond lengths, bond angles, and atomic positional and thermal parameters, ^1H NMR NOEDIFF experiment for **3**, and a view of the structure of **3** down the P-Ir-P axis with the phenyl substituents removed for clarity (11 pages). Ordering information is given on any current masthead page.

(18) In ref 13, the structures of the methyl alkyl complexes **3** and **4** are drawn as square pyramidal; this was our perception before we isolated the dimethyl derivative **2**, with its simple ^1H NMR spectrum, and before we had accumulated the NOE results.

Circular Dichroism of the Backbone and Side Chains Separated from Natural Circular Dichroism of Poly-L-tryptophan by the Fluorescence Detected Circular Dichroism Method

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Peggion and co-workers have concluded that poly-L-tryptophan (PLT) adopts a right-handed α -helical conformation in 2-methoxyethanol (2 ME).^{1,2} The circular dichroism (CD) and optical rotatory dispersion (ORD) information presented by them indirectly suggests an α -helix of PLT in 2ME. However, it is difficult to assign directly a backbone conformation of PLT on the basis of the shape of the CD or ORD spectrum, as it contains side-chain contributions.

We succeeded in separating CD depending on the backbone contribution and on the side-chain contributions from natural CD of PLT (an average degree of polymerization of 30) in 2ME using the fluorescence detected circular dichroism (FDCD) technique, which was used to obtain the CD of a fluorescent chromophore.^{3,4}

As a result, the shape of the separated backbone CD spectrum directly verified that PLT is α -helical in 2ME.

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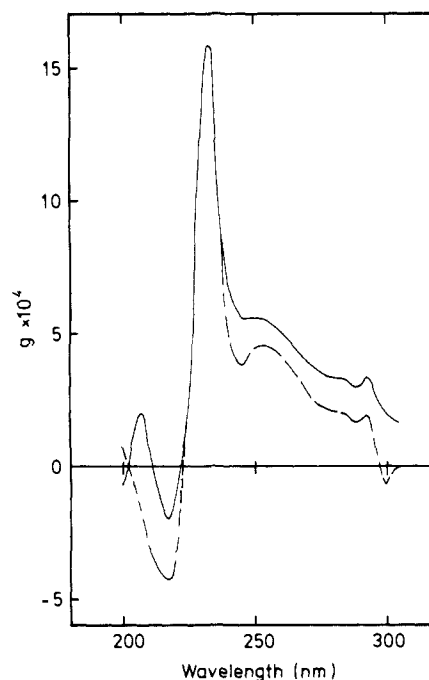


Figure 1. Spectra of fluorescence dissymmetry factor g_f (—) and absorption dissymmetry factor g_a (---) of PLT in 2ME. Error limits are roughly $\pm 5 \times 10^{-5}$.

We report herein the conformational analysis of PLT using the FDCD method and significant information concerning the optical activity of PLT.

FDCD experiments were performed by using a JASCO J-500C spectropolarimeter, setting a solution filter (a 100-mm thickness of saturated aqueous solution of NaNO_3) between the sample cell and the photomultiplier for the elimination of the exciting circularly polarized light. The FDCD spectrum was obtained by scanning eight times with a 8-s time constant and averaging, using a JASCO DP-501 data processor. The spectra measurements were taken 3 times in a 0.5- or 1.0 mm-pathlength cuvette, and the obtained spectra were in good agreement with each other within the limit of experimental error. The FDCD base lines were measured with indole in 2-ME or DL-tryptophan in H_2O at pH 10. These base lines were coincident, and no base-line shifts were observed. PLT fluorescence was essentially depolarized ($P < 0.06$) below 295 nm.

Figure 1 compares the fluorescence dissymmetry factor g_f obtained from the FDCD experiments with the absorption dissymmetry factor g_a obtained from the ultraviolet absorption and CD spectra. The distinction between the shapes of these two dissymmetry factor spectra indicates that the separation of CD of its fluorophores from natural PLT CD have been accomplished by the FDCD technique.

It is reasonable to consider that PLT optical activity may originate from a one-electron mechanism μ_1 -ml; the electric and magnetic-dipole transitions of the chromophore, such as indole chromophores $^1\text{B}_a$, $^1\text{B}_b$, $^1\text{L}_a$, $^1\text{L}_b$ and amide chromophores n - π^* , π - π^* , are mixed by the static Coulombic field of the other groups, and from a dynamic coupling mechanism μ_1 - μ_2 ; electric dipole interactions of amide-amide, amide-indole, and indole-indole chromophores.^{5,6}

However, on the following assumptions we tried to separate the backbone CD, coming from amide chromophore contributions, and the side-chain CD, coming from indole chromophore contributions, from natural CD of PLT using the eq 1 and 2.

$$\Delta\epsilon_{\text{side}} = g_f \epsilon_{\text{PLT}} \quad (1)$$

$$\Delta\epsilon_{\text{back}} = \Delta\epsilon_{\text{PLT}} - \Delta\epsilon_{\text{side}} \quad (2)$$

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